CRYSTAL GLASS MATERIALS BASED ON CATALYZED CORDIERITE GLASS SYNTHESIZED UNDER EXPOSURE TO CONCENTRATED RADIANT FLUX

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The results of investigations of crystal glass materials based on cordierite glass containing TiO_2 as a catalyst are presented. It is established that the synthesis of glass under exposure to a concentrated radiant flux has the same effect on crystallization processes as increasing the catalyst content. The optimal composition and conditions for obtaining sintered sitals from glass powder are determined.

Key words: crystal glass materials, catalyst, crystallization, radiant flux

There are a large number of works on the particularities of the crystallization of $MgO – Al_2O_3 – SiO_2$ glasses. These works devote special attention to the crystallization of glass with cordierite composition, since it is precisely this type of glass that forms the base for crystal glass materials with the optimal combination of dielectric and thermomechanical properties. Cordierite crystallizes via the formation of a number of intermediate phases whose temperature intervals of formation and stability depend on a number of factors, including the conditions under which the glasses are synthesized. This article presents the results of investigations of the character of the crystallization of glass with cordierite composition obtained under exposure to a concentrated radiant flux.
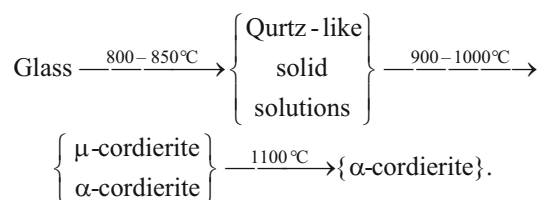
The initial components were magnesium and aluminum oxides as well as quartz-kaolinite-pyrophyllitic rock (SiO_2 source). Chemical analysis showed this mineral to contain the following (%[2]): 77.64 SiO_2. 17.43 Al_2O_3, 0.39 MgO, and trace impurities (Fe_2O_3, Na_2O, K_2O).

The glasses were synthesized in a solar furnace as well as in a simulator where 10-kW xenon lamps served as the source of heat. The fused glass was poured into water. This method of quenching the melt made it possible to obtain brittle granules which could be easily milled.

A DRON-UM1 diffractometer was used for x-ray phase analysis and a Q-1500 D derivatograph differential-thermal analysis. Glass powders with different particle size (from 1 – 5 to 80 μm) as well as 2 – 3 mm fragments of granules were analyzed.

Previous investigations of glasses with stoichiometric cordierite composition without catalysts [1, 2] showed that the crystallization process can be represented in terms of the following scheme:

$$\text{Glass} \xrightarrow{800-850\,°C} \left\{ \begin{array}{c} \text{Qurtz - like} \\ \text{solid} \\ \text{solutions} \end{array} \right\} \xrightarrow{900-1000\,°C}$$

$$\left\{ \begin{array}{c} \mu\text{-cordierite} \\ \alpha\text{-cordierite} \end{array} \right\} \xrightarrow{1100\,°C} \{\alpha\text{-cordierite}\}.$$

Since glass cannot undergo bulk crystallization without a catalyst, investigations were performed to determine the influence of TiO_2 as a catalyst on the crystallization process for glass with cordierite composition. The catalyst was introduced into the stoichiometric glass in amounts 2 – 12% (above 100%). It was determined that when TiO_2 was introduced during the melting process the color of the castings ranged from straw-colored (2% TiO_2) to black (12% TiO_2), which could indicate an increase of the Ti^{3+} content in the glass.

The introduction of 2% TiO_2 had no appreciable effect on the crystallization rate of the glass. The main crystalline phase was α cordierite. As the amount of TiO_2 increased, the crystallization process changed sharply. The crystallization of μ cordierite was already activated during sintering of

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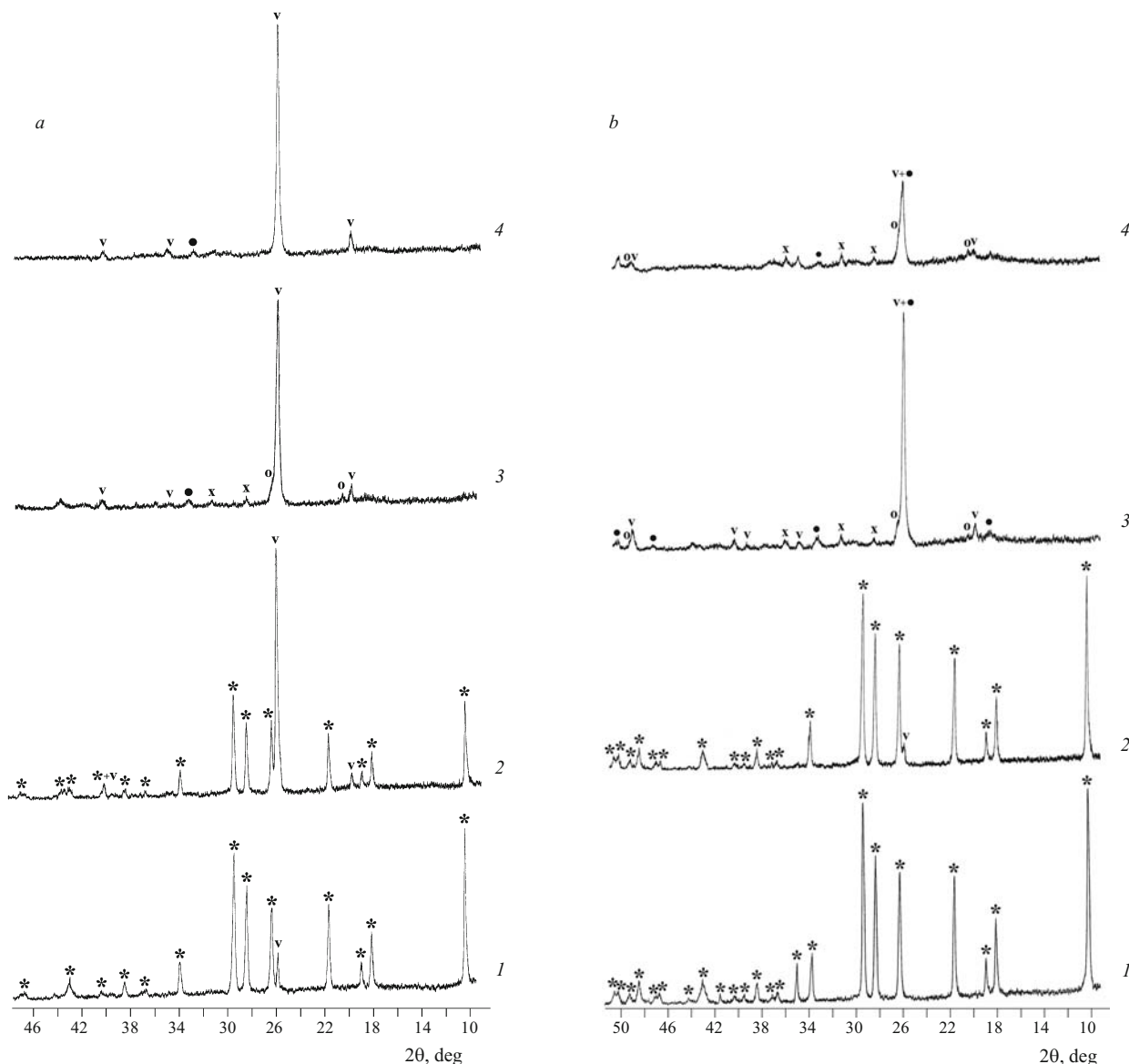[2] Here and below — content by weight.

Fig. 1. Diffraction patterns of cordierite glass samples with TiO_2 addition, sintered at 920°C (*a*) and 1020°C (*b*): *1, 2, 3,* and *4*) TiO_2 content, respectively, 2, 5, 10, 12%; ★) α cordierite; **v**) μ cordierite; O) quartz; ●) solid solution $nAl_2TiO_5 \cdot mMgTi_2O_5$; **x**) enstatite.

coarse-grain samples at 920 and 1020°C (Fig. 1). According to XPA the largest amount of μ cordierite is observed in samples with 10% TiO_2. As the TiO_2 content increases to 12%, strong diffuseness and low intensity of the peaks are observed in the diffraction patterns. The DTA data show the crystallization temperature of α cordierite to be dependent on the TiO_2 content (Fig. 2).

When TiO_2 was present in the glass, the differential thermograms were different from those of stoichiometric glass.

In first place, the shape and size of the peaks corresponding to the exothermal effects due to the crystallization of μ and α cordierite changed. The ratio of the areas of the exo-effects $S_\alpha / S_\mu \geq 1$ in the absence and ≤ 1 in the presence of

the TiO_2 catalyst with the glass synthesized under identical conditions; this shows that the crystallization of μ cordierite intensifies and the crystallization of α cordierite is suppressed. XPA confirmed these data. In the presence of 10 and 12% catalyst the transition of μ into α cordierite was completed during sintering for 6 h at temperatures above 1100°C, while in titanium-free stoichiometric glass this transition was completed at lower temperatures (980 – 990°C).

It is known [3 – 5] that the influence of TiO_2 is due to the presence of aluminum-titanium complexes which are formed as a result of liquation processes. If in the absence of TiO_2 and for low concentrations of TiO_2 cordierite is formed as a result of recrystallization of μ cordierite (or quartz-like solid
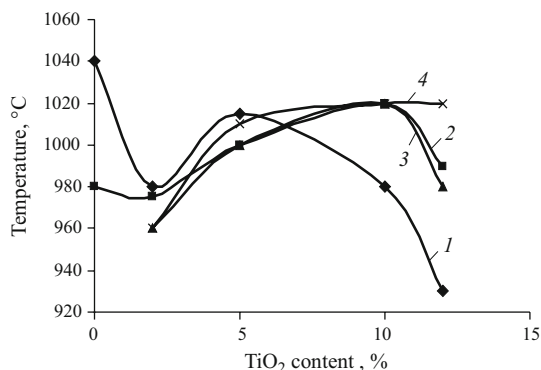
Fig. 2. Crystallization temperature of α cordierite versus the TiO$_2$ content for powders with different particle size: *1*, *2*, *3*, and *4*) particle size 2 – 3 mm, 80 – 40, < 40 and 1 – 5 μm, respectively.
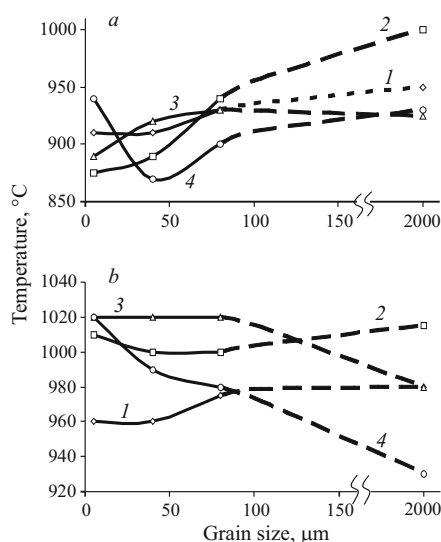

Fig. 3. Crystallization temperature of μ (*a*) and α (*b*) cordierite versus the particle size for glass with different TiO$_2$ content: *1*, *2*, *3*, and *4*) 2, 5, 10, and 12% TiO$_2$, respectively.

solutions) directly into α cordierite, in the presence of TiO$_2$ the reaction proceeds according to a more complicated scheme with different intermediate crystalline phases being formed. It could be that this is why the crystallization temperature of cordierite is higher in the presence of substantial TiO$_2$ concentrations.

Just as in glass with no catalysts, μ and α cordierite peaks in the differential thermograms split as the particle sizes in titanium-containing glass powders decrease. The temperature difference between the corresponding exo-effects arose primarily because the crystallization temperature of μ cordierite decreased while $\Delta t_{\text{exo}(\alpha)}$ changed to a lesser degree. The strongest shift occurred at the transition from coarse-grain (2 – 3 mm) to fine-grain (80 – 40 μm) samples. As the particle size in the experimental powders decreased

further (< 40 and 1 – 5 μm) the shift was 0 – 10°C and the dependence of the crystallization temperature of μ and α cordierite on the glass particle size was nonmonotonic (Fig. 3).

According to the XPA data, the amount of μ cordierite in samples with 5 and 10% TiO$_2$ and α cordierite with 12% TiO$_2$ increased in glass powders (80 – 40 and < 40 μm) crystallized at 1020°C. It should also be noted that when the catalyst was added, aside from the main crystalline phase mentioned above, magnesium aluminum titanate was also observed and its content increased with increasing TiO$_2$ content. In addition, cristobalite, spinel, and (or) enstatite were present in the diffraction patterns. As the powder particle size (1 – 5 μm) and sintering temperature increased, these phases vanished simultaneously with the activation of α cordierite formation. At higher temperatures (1200 – 1350°C) the transition from μ to α cordierite was completed and magnesium aluminum titanate decomposed with rutile being precipitated.

The results obtained agree quite well with the published data [3, 4]. This character of the phase transformations preceding the formation of cordierite is due to the TiO$_2$-induced change of the structure of the glass and the position of the composition in the phase diagram. In the materials investigated the ratio of the aluminum, magnesium, and silicon oxides changed when TiO$_2$ was introduced. Since some MgO and Al$_2$O$_3$ enters into reaction with TiO$_2$ with magnesium aluminum titanate being formed, the composition obtained shifts in the phase diagram from the line MgO : Al$_2$O$_3$ = 1 into a region with higher SiO$_2$ content and lower Al$_2$O$_3$ content. For glass with 12% TiO$_2$ it corresponds to the ratios MgO : Al$_2$O$_3$: SiO$_2$ = 24.62 : 13.81 : 61.57, provided that all of the TiO$_2$ participates in the formation of the titanate. Comparing the differential thermograms of the synthesized systems containing the catalyst with the glass compositions which we studied previously — 21.44% MgO, 21.49% Al$_2$O$_3$, 57.07% SiO$_2$, 15.06% MgO, 27.80% Al$_2$O$_3$, and 57.14% SiO$_2$ — without the catalyst showed the identical ratio of the intensities of the μ and α cordierite exo-effects.

At the same time a discrepancy was found in the determination of the optimal concentration of the catalyst as compared with the results obtained by other investigators. In [5] it was established that 12 – 15% TiO$_2$ is the optimal content for sitallization of glass with cordierite composition. The curves of the crystallization temperature versus the amount of TiO$_2$ contain an inflection point at 10% TiO$_2$ content for α cordierite and 12% quartz-like solid solutions (in our case μ cordierite).

Our results have shown that the inflection point has shifted toward lower TiO$_2$ content. The maximum content of μ cordierite is observed in the interval 5 – 10%, and at 10% its content did not change with decreasing particle size, indicating bulk crystallization of μ cordierite, but α cordierite precipitated at higher temperatures. In our opinion this is due to the influence of the conditions of synthesis, which pro-

mote partial reduction of Ti^{4+} to Ti^{3+}. The Ti_2O_3 formed in this case, stabilizing the aluminum and magnesium-titanate complexes, have the same effect on the structure of the glass and the process resulting in its crystallization as does an increase of the TiO_2 content. As higher Ti_2O_3 concentrations the TiO_2 content in the glass decreases. A change in the position of Ti^{3+} in the structure of the glass starts to play the main role in pre-crystallization liquation; this also intensifies liquation processes [5]. Depending on the Ti_2O_3 and TiO_2 ratio, either μ or α cordierite undergoes bulk crystallization.

We also determined that the fineness of the catalyzed glass had a large effect on its crystallization process. As fineness increased, the process resulting in the formation of μ cordierite was activated in glasses which are not prone to bulk crystallization. However, further reduction of the glass grains to sizes less than 5 μm nullifies this effect. In glasses with bulk crystallization of α cordierite (12% TiO_2) the activation of the process started at smaller particle sizes (80 – 40 μm) of the glass powder in the temperature interval 1000 – 1100°C. Apparently, oxidation of Ti^{3+} to Ti^{4+} occurred on the surface of the particles during the sintering of fine glasses.

In choosing the optimal catalyst concentration for obtaining sintered sitals with prescribed properties was chosen, in addition to a definite phase composition being formed the highest possible degree of sintering of the glass powders had to be attained.

Water absorption by the samples was chosen to characterize the degree of sintering. It was determined that sintering started only in samples where the transition from the metastable modification of cordierite to the stable α form was completed. However, complete sintering did not occur even at quite high temperatures, irrespective of the composition of the glass. The water absorption of sintered glass powders was at least 14 – 15%. At the same time, to obtain sitals with the highest possible characteristics, specifically, with zero water absorption, it was necessary to continue the investigations in order to optimize heat-treatment regimes.

It is known that pre-crystallization heat-treatment changes the phase composition, structure, and therefore the properties of sitals. We tested different multistep sintering regimes. The temperatures t_1 at the first step were chosen on the basis of the DTA data. They corresponded to the temperatures of different sections of the curve of the first exo-effect (500 – 800°C) as well as the second exo-effect, which precedes the crystallization of α cordierite (about 980°C). The temperature t_2 of the second heat-treatment step was 1020°C initially.

Granulated glass and cordierite glass powders with 2 – 12% TiO_2 were subjected to crystallization in prescribed heat-treatment regimes. At 2% TiO_2 changing the heat-treatment regimes had no noticeable effect on the character of the crystallization of glass. As the catalyst content in the glass increased, the influence of pre-crystallization heat-treatment increased.

Heat-treatment of granulated substances during the pre-crystallization period (500 – 800°C) lowered the temperature of the phase transitions: the temperature of the $\mu \to \alpha$ cordierite transition for glass containing 5% TiO_2 and the temperature of μ cordierite decomposition at 10 and 12% TiO_2. This process accelerated when t_1 increased from 600 to 770°C. The amount of magnesium aluminum titanate was observed to increase at the same time.

As expected, pre-crystallization treatment improved the sintering of glass powder. The water absorption of the samples decreased by a factor of 2 as compared with single-stage sintering at 1020°C for 6 h. At the same time, at the indicated temperature of the final stage of heat-treatment it was impossible to achieve more complete sintering for which the samples possess zero water absorption. Consequently, the temperature of the final stage of heat treatment was increased to 1350°C (1 h).

The phase composition of the sintered samples was determined at the same time that the completeness of sintering was monitored. Analysis of the dependence of the completeness of sintering on the phase composition of the crystallized glasses showed that there exist several ranges of values of water absorption which are determined by the form of the crystalline phases. Sintering was practically nonexistent (water absorption 25 – 30%) when the crystalline phases are represented by μ cordierite and quartz-like solid solutions. Sintering improved for crystallization of samples containing α cordierite; water absorption decreased to 10 – 20%. The presence of titanium-containing phases in the form of magnesium aluminum titanate did not appreciably improve the sintering. The process was activated when this compound decomposed with rutile being formed in the process. In this case water absorption decreased to 0 – 8%. For this phase composition the amount of the glass phase determined by the heat-treatment regimes has a considerable influence. Its content should not exceed 10 – 15%. Otherwise, a sharp increase of the amount of the glass phase to 25 – 30% resulted in deformation of the sintered samples subjected to heat-treatment in a regime with $t_1 = 600$°C and $t_{max} = 1350$°C. The preferred temperature for the first stage of heat treatment was 980°C with the temperature of the final stage remaining the same.

Thus, pre-crystallization heat-treatment of cordierite glass as a function of the TiO_2 amount decreases the temperature of the phase transitions and stabilizes the titanium-containing phase.

The dense sintered crystal glass materials can be obtained from glass synthesized under exposure to a concentrated radiant flux is possible under the following conditions:

cordierite glass containing 12% TiO_2 is used;

a two-stage heat-treatment regime with the temperatures 980 and 1250°C at the first and final stages, respectively, is used;

the crystalline phases must be represented by α cordierite and rutile; and,

the amount of the glass phase should not exceed 10 – 15%.

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